Workshop ABINIT_{02}

From Total Energies to Curie Temperatures

(with ABINIT and VASP)

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Ferromagnetic semiconductors

From DFT to Heisenberg model

Percolation theory for T_c

ABINIT vs. VASP

Self-compensation and T_c

What are ferromagnetic semiconductors?

Prehistory

- 1960s: Crystalline FM semiconductors; transition-metal chalcogenides, spinels

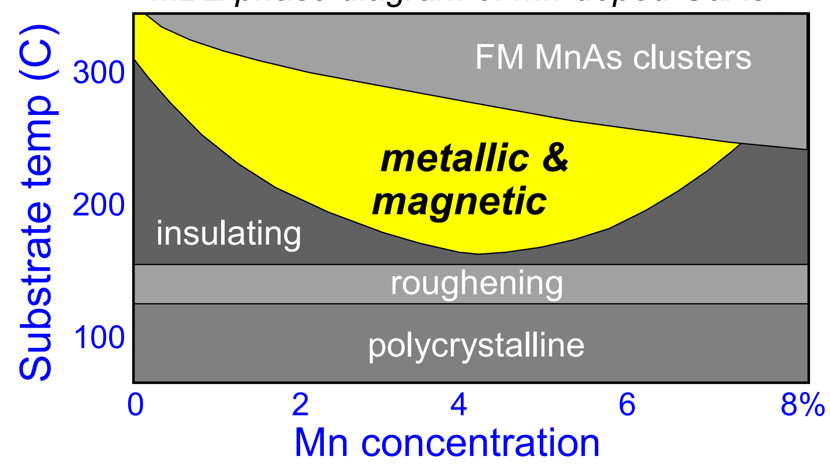
Ancient history

- 1980s: Dilute Magnetic Semiconductors based on II-VI hosts; Mn-doped CdTe

Ferromagnetic DMS's

- 1989: Mn-doped InAs (IBM)
- 1996: Mn-doped GaAs (Tohoku)
- 2000: Mn-doped Ge (NRL)

MBE phase diagram of Mn-doped GaAs



All new!

Non-volatile character
plus
Wavefunction engineering

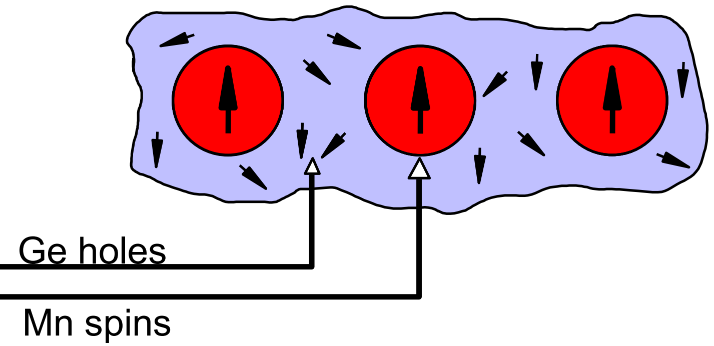
Caveats

- Curie temperatures limited to 120 K
- Limited to *p*-type conduction; *n*-type needed

Ferromagnetism from indirect exchange

The Zener Model for ferromagnetic semiconductors

$$H = H_0 + J_{pd} \sum \vec{S}_I \cdot \vec{s}_i$$



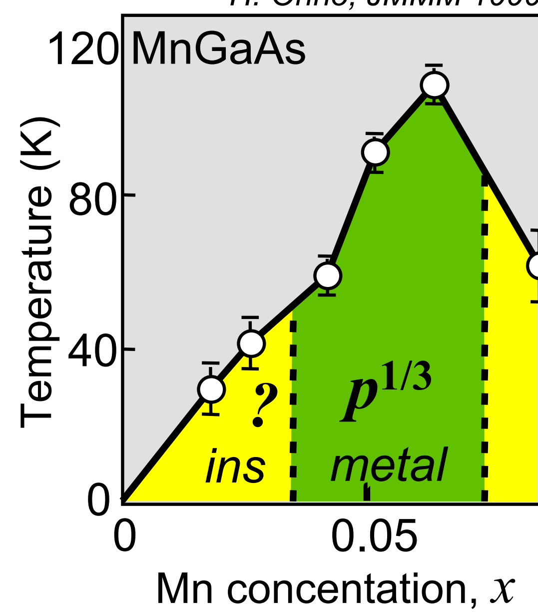
Important points

- Ge(p)-Mn(d) hybridization $\Rightarrow J_{pd} > 0$ (Antiferromagnetic)
- Effective interaction between Mn spins is Ferromagnetic
- Mn provide both spins, x, and holes, p

Mean-field Curie temperature for Mn_xGe_{1-x}

$$T_c \propto J_{pd}^2\, x\, p^{1/3}\, S(S+1)$$

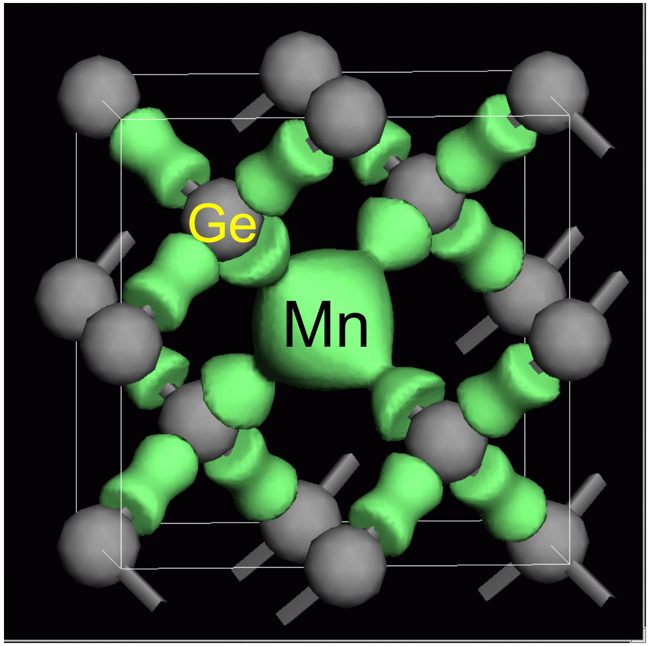
H. Ohno, JMMM 1999



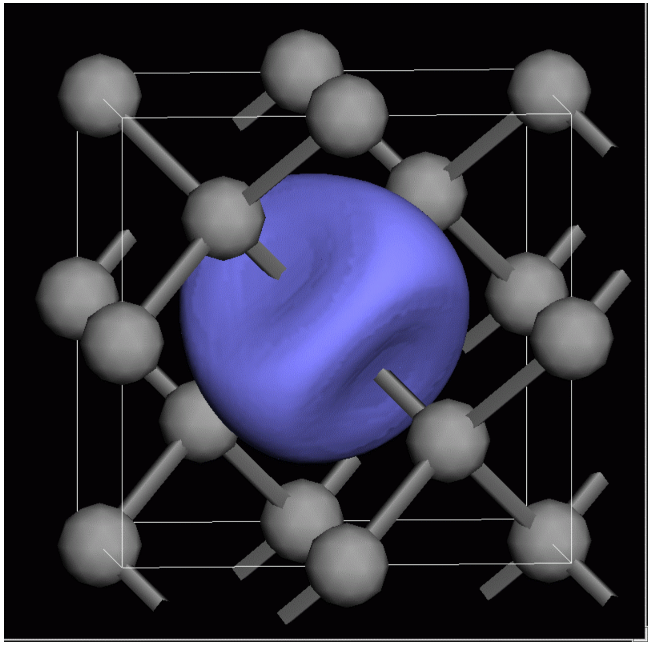
Elemental FM semiconductor, Mn_xGe_{1-x}

Y.D. Park, A. Hanbicki, S.C. Erwin, C.S. Hellberg, J.M. Sullivan, ..., B.T. Jonker, *Science* **295**, 651 (2002)

Valence electron density



Electron spin density



Density Functional Theory

- Mn strongly prefers the substitutional site
- Surrounding Ge lattice nearly undistorted (< 2% bond strain)
- Spin density completely localized around Mn

From DFT to the Heisenberg model

Two Mn atoms in Ge supercell

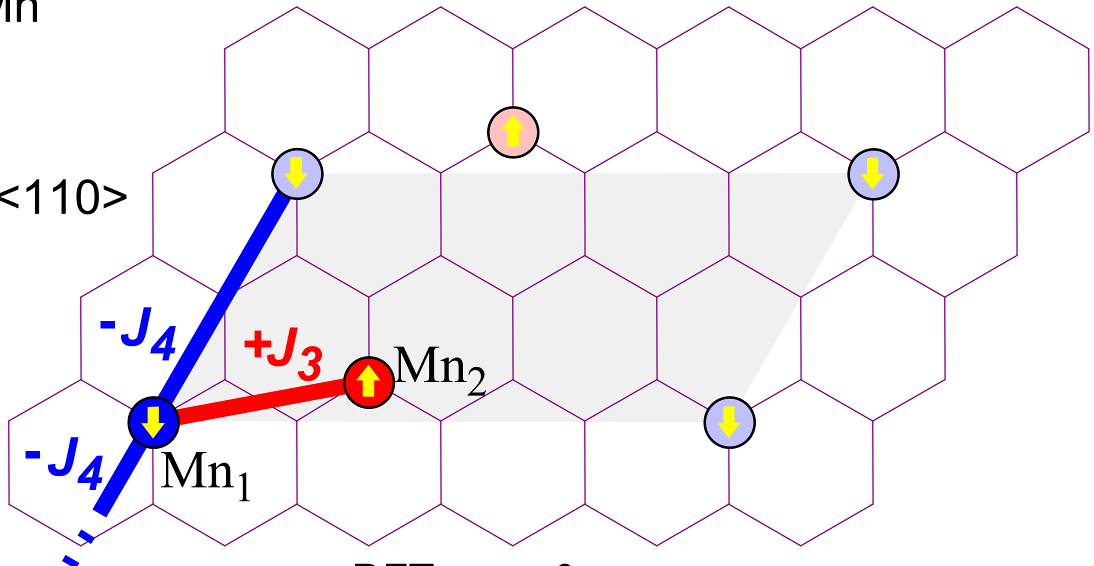
- 4×2×2 ⇒ 32 atoms, i.e. 6% Mn

DFT total energies

- 4 arrangements of Mn along <110>
- 2 spin configurations

Heisenberg Hamiltonian

$$H = E^0_{ij} - \sum J_{ij}\, \vec{S}_i \cdot \vec{S}_j$$

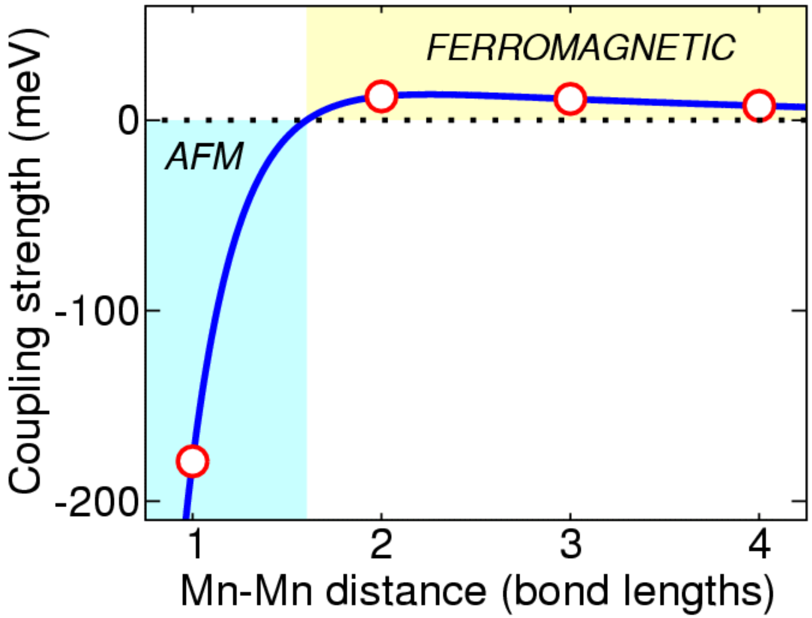


$$E^{\mathrm{DFT}} = E^0_3 + J_3 - 6J_4$$

Coupled linear equations

- ⇒ Spin coupling constants, J_n
- ⇒ Chemical energies, E^0_n

Spin coupling constants



DFT coupling constants

J_1	−179.1 meV
J_2	+12.4
J_3	+11.1
J_4	+7.6

Four-parameter fit

$$J(r) = J_{AF} \exp(-r/R_{AF}) + J_{FM} \exp(-r/R_{FM})$$

Competing interactions $\Rightarrow R_{AF} = 0.5$ Å, $R_{FM} = 5.0$ Å

Strong short-range AFM competing with weak long-range FM

Ferromagnetic phase transition

Mean-field theory assumptions

- Each spin interacts with many
- Interaction range >> spin radius

MnGe exp'tal concentrations

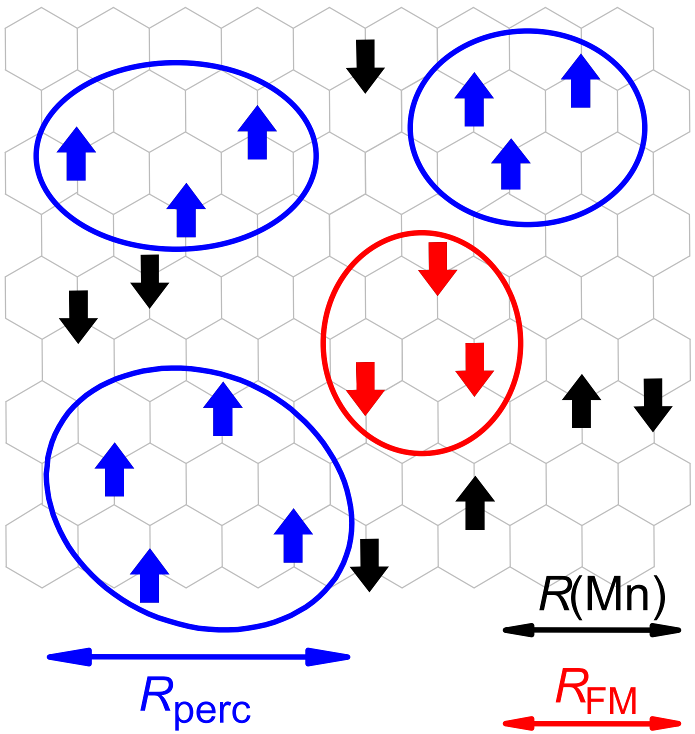
- Ferromagnetic range R_{FM} = 5.0 Å
- Average Mn separation comparable: R(Mn) ~ $1/x^{1/3}$ (4.6 Å for x=0.05)

Percolation theory for T_c

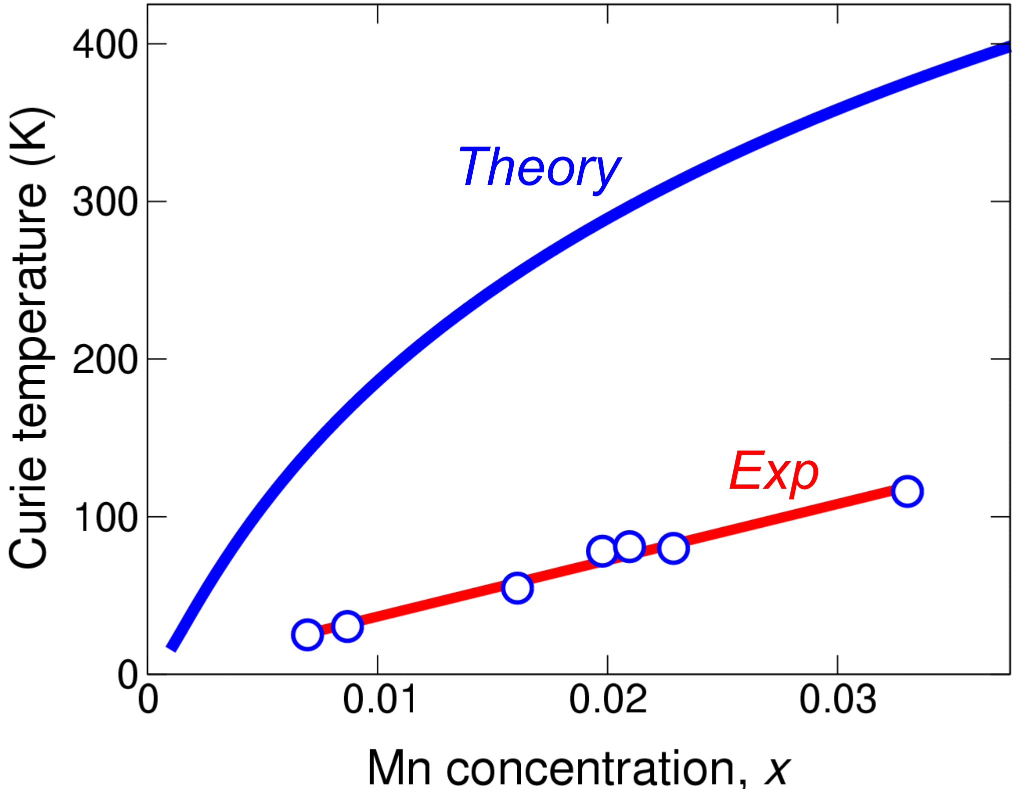
Ferromagnetic transition occurs when FM clusters reach $R_{perc}=1.34\ R(\mathrm{Mn})$.

Coupling strength then determines T_c according to:

$$k_B T_c = S(S+1)\ J(R_{perc})$$

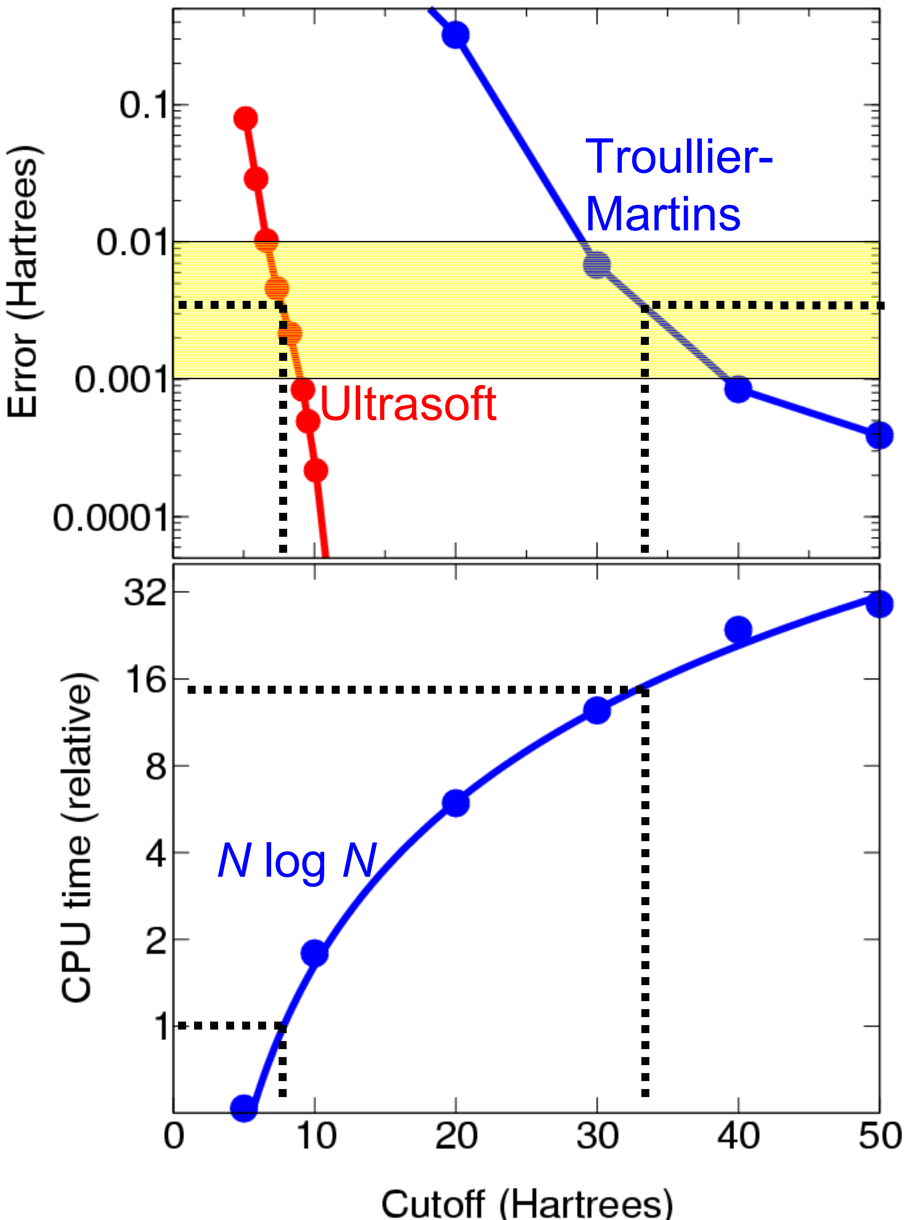


Curie temperature vs. Mn concentration



1. Known tendency of LDA to overestimate *J* (by 3-6)
2. Strong crystallographic anisotropy of $J(\vec{R})$
3. Hole compensation (in the material, but not in DFT)

ABINIT vs. VASP

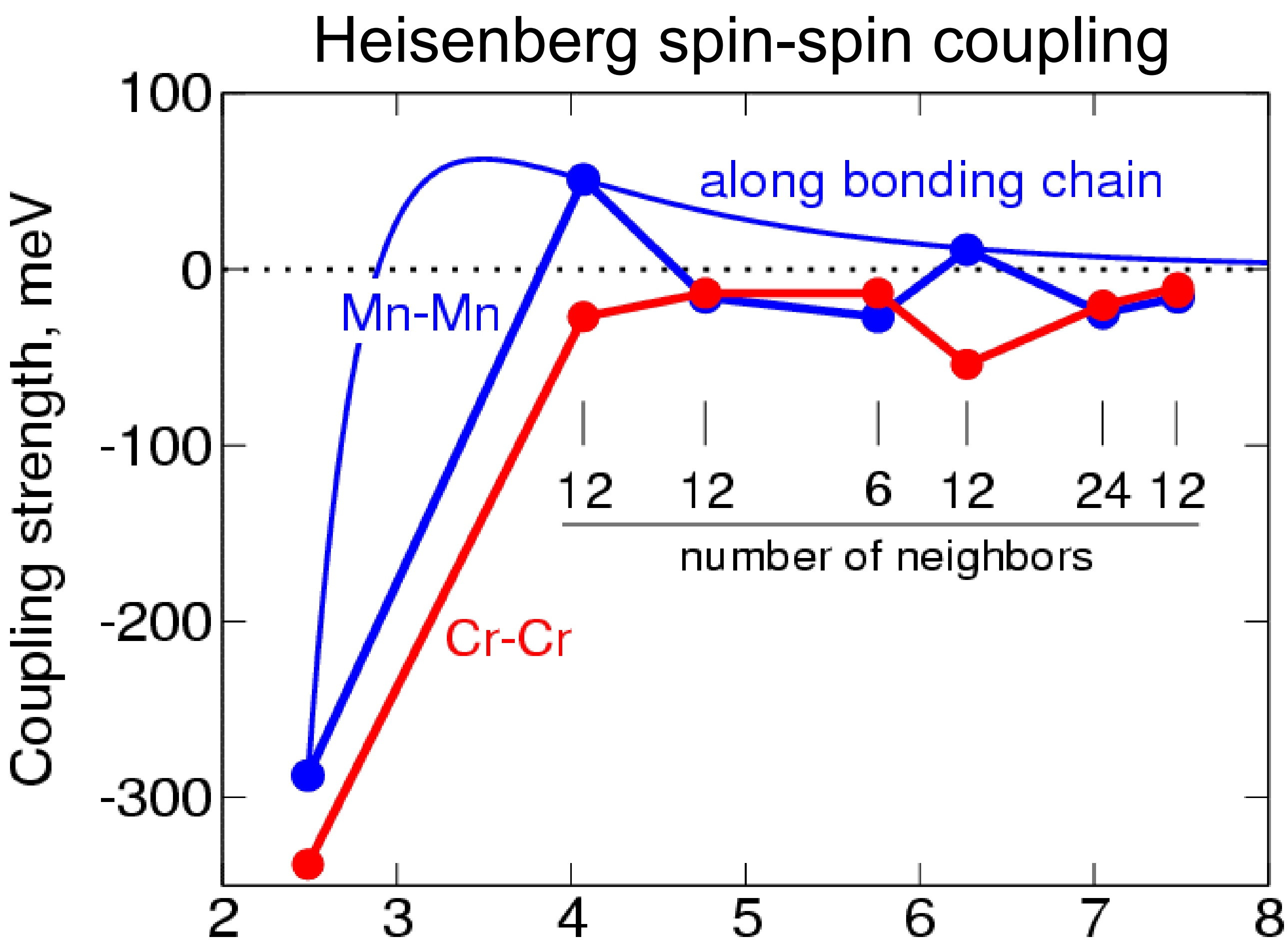


Soft vs. ultrasoft psp's

- Test: Total energy of Mn_1Ge_{15}
- ABINIT: Troullier-Martins (*.pspnc)
- VASP: Ultrasoft (PAW is similar)

- CPU time dominated by FFT
- Ultrasoft advantage > factor 10 (!)

Spin coupling constants, revisited



- 128-atom supercells
- DFT total energies
- Pseudopotentials

MnGe

FM beyond n.n.

FM and AF up to 8 Å

CrGe

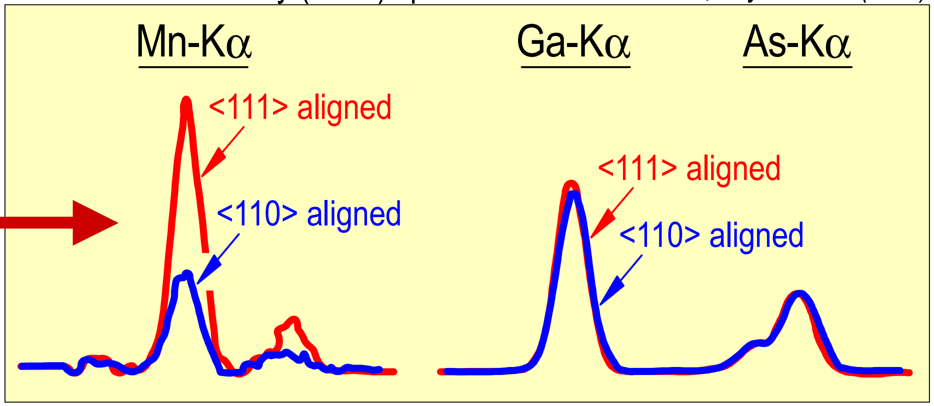
AF everywhere ⇔ exp

Large crystallographic anisotropy can make FM-vs-AF competition more important than previously suspected

Compensation by Mn interstitials

S.C. Erwin & A.G. Petukhov, PRL (2002)

Particle-induced x-ray (PIXE) spectra *Yu et al., Phys. Rev. B (2002)*

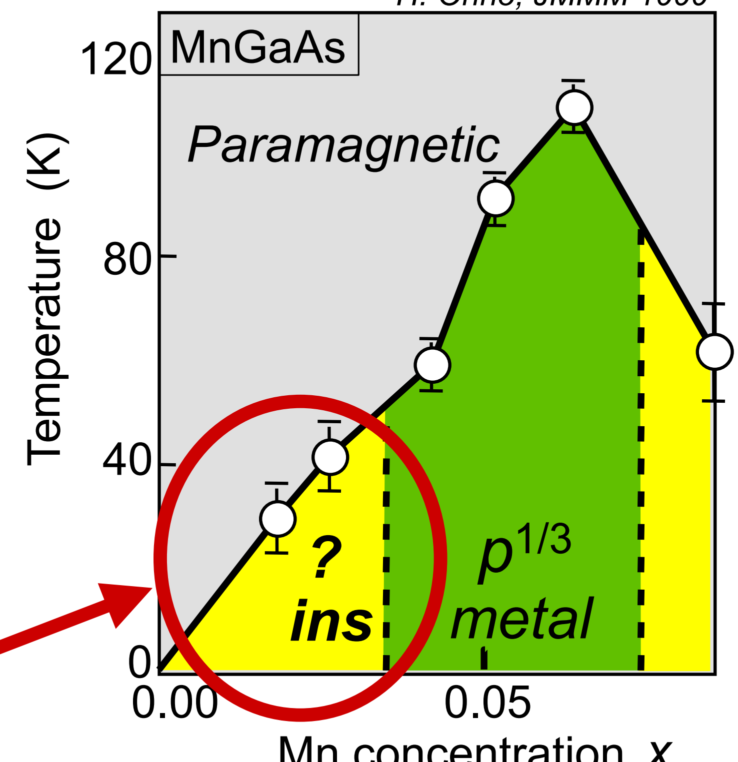


Photon energy

Experimental findings

- Compensation: MnGaAs, MnGe
- Ion channeling ⇒ Interstitial Mn!
- Exp'l correlation: $T_c \Leftrightarrow p \Leftrightarrow x_{int}$

H. Ohno, JMMM 1999

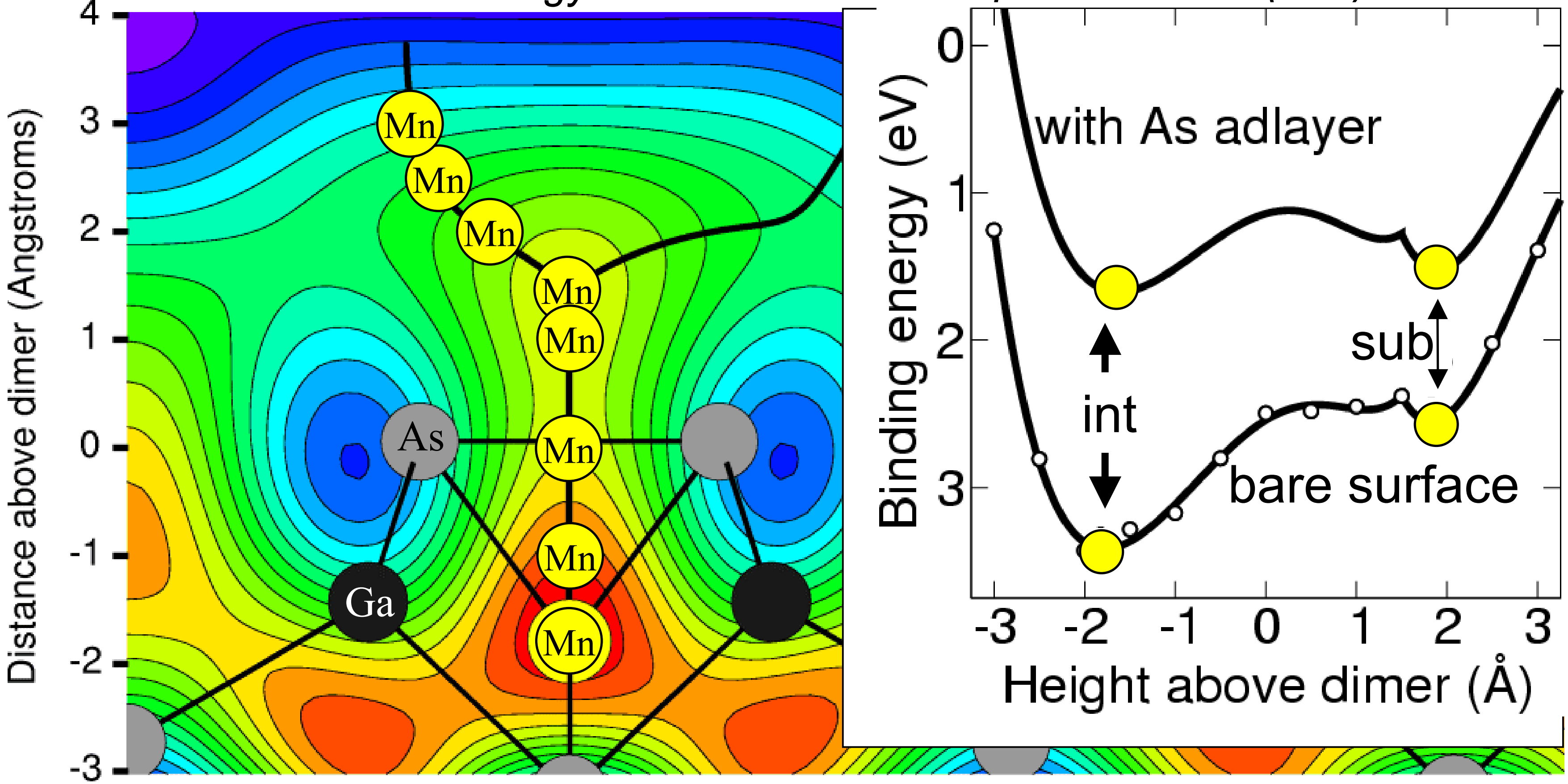


Questions for theory

1. How/why are interstitials formed?
2. What determines relative abundance of substitutional and interstitial Mn?
3. Under what conditions do interstitials compensate?
4. What role does compensation play in the ferromagnetism?

Interstitials form during MBE growth

Potential-energy surface for Mn adsorption on GaAs(001)

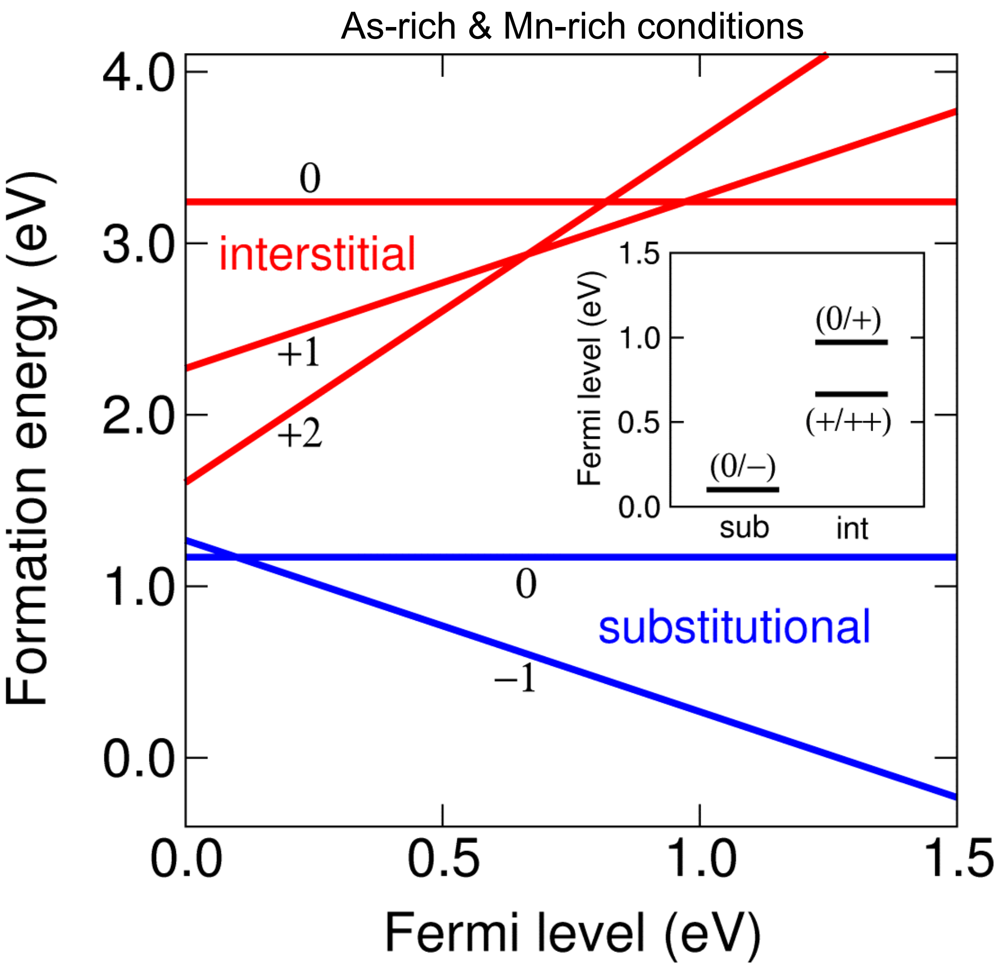


Adsorption at low temperature leads to substitutional <u>and</u> interstitial Mn

Electrical activity of Mn impurities

Formation energy

$$E_t\,[\mathrm{Mn}^q] - n_{Ga}\mu_{Ga} - n_{As}\mu_{As} - \mu_{Mn} + qE_F$$



- Substitutional Mn is a *single acceptor*
  - Ionization energy = 100 meV
  - Exp. ionization energy = 113 meV
- Interstitial Mn is a *double donor*

Each interstitial compensates two substitutional Mn impurities

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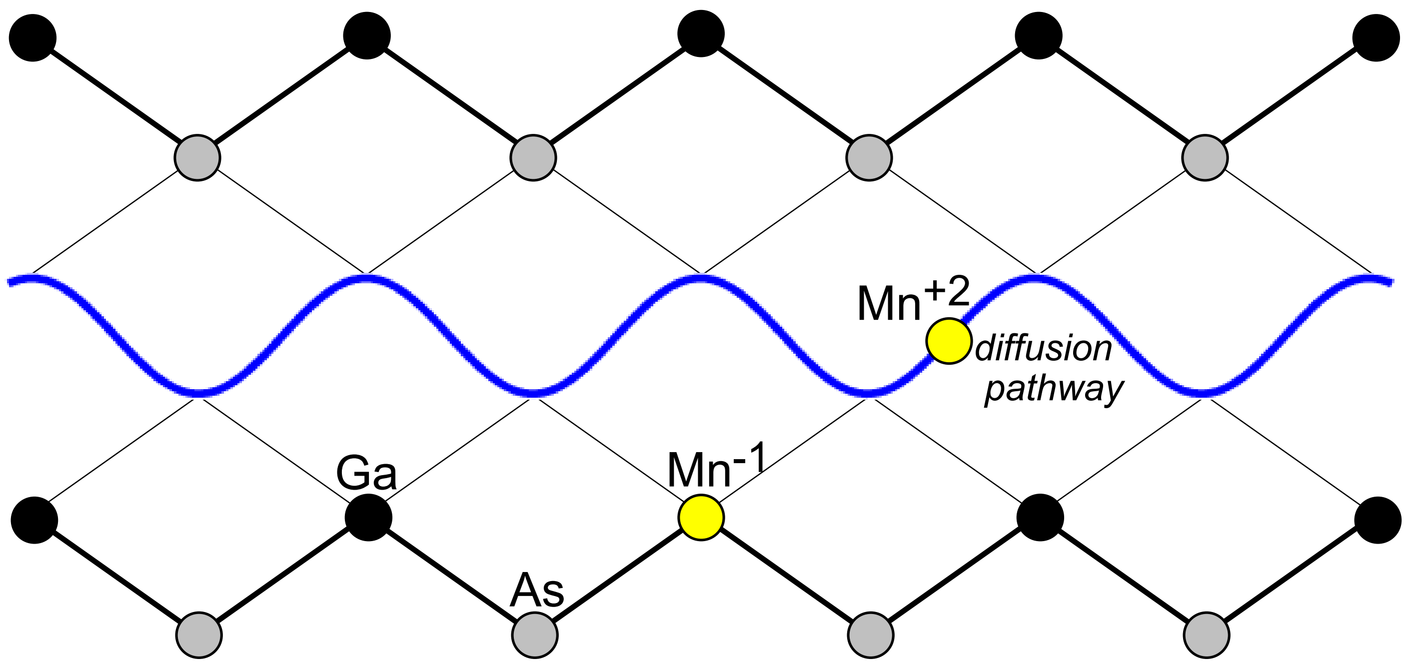
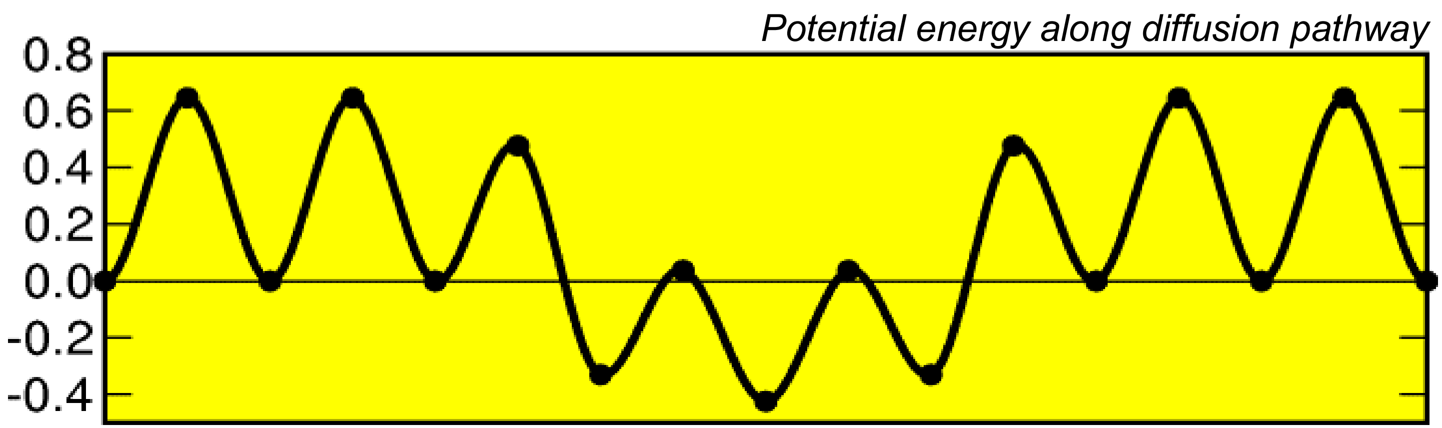
If 1/3 of the Mn is interstitial, material is completely compensated

What prevents interstitials from escaping?





Consequences for magnetism

Zener Model revisited

$$H = \sum t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} - J_{pd} \sum \vec{S}_i \cdot \vec{s}_i + \sum \varepsilon_i a^{\dagger}_{i\sigma} a_{i\sigma}$$

Hopping of holes between Mn spins

Exchange coupling between Mn spin and hole

Fluctuations in on-site energies due to neutral and charged acceptors, Mn^0 and Mn^{-1}

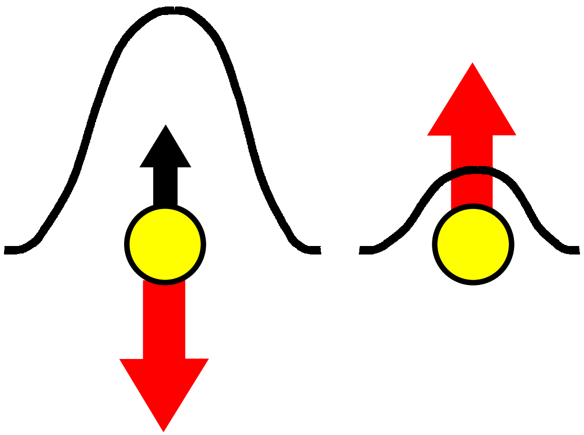
2nd-order perturbation theory

Effective Heisenberg interaction

$$H = \sum \frac{|t_{ij}|^2}{\varepsilon_i - \varepsilon_j} (q_i - q_j) \left(1 + \frac{\vec{S}_i \cdot \vec{S}_j}{S(S+1)}\right)$$

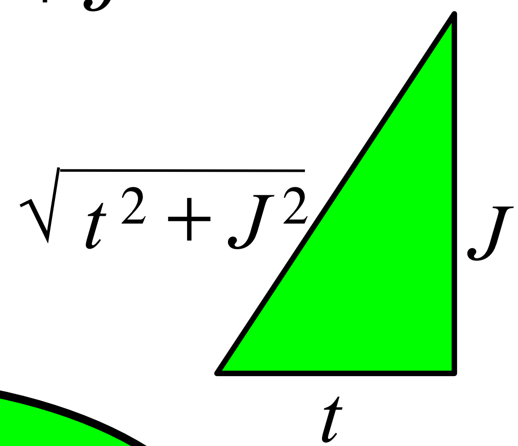
$\Rightarrow$ *Ferromagnetic interaction survives only between Mn^0 and Mn^{-1}!*

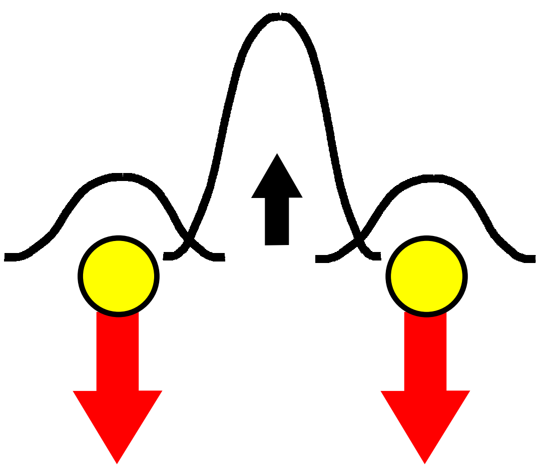
Toy model: Two Mn atoms sharing one hole



Antiferromagnetic

$$E_{\mathrm{AF}} = -\sqrt{t^2 + J^2}$$

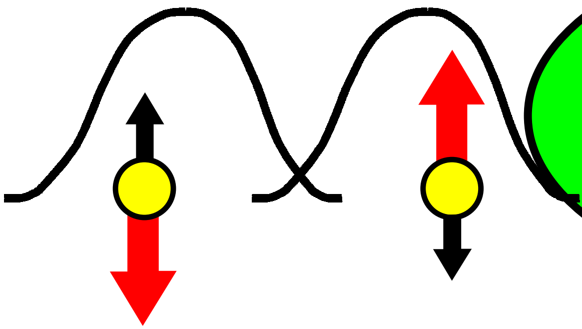




Ferromagnetic

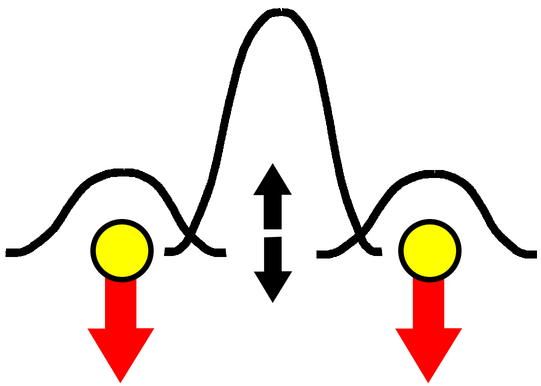
$$E_{\mathrm{FM}} = -|t| - |J|$$

Toy model: Two Mn atoms sharing <u>two</u> holes



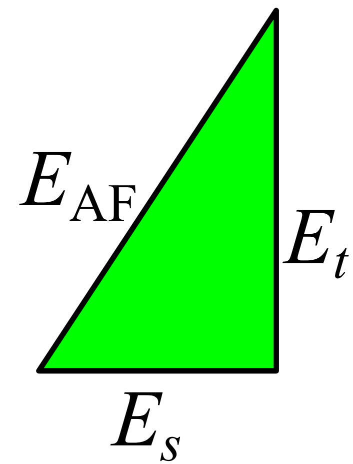
Antiferromagnetic

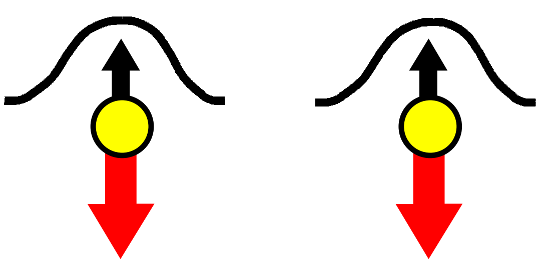
$$E_{\mathrm{AF}} = -2\sqrt{t^2 + J^2}$$



Ferromagnetic singlet

$$E_t = -2\,|t|$$



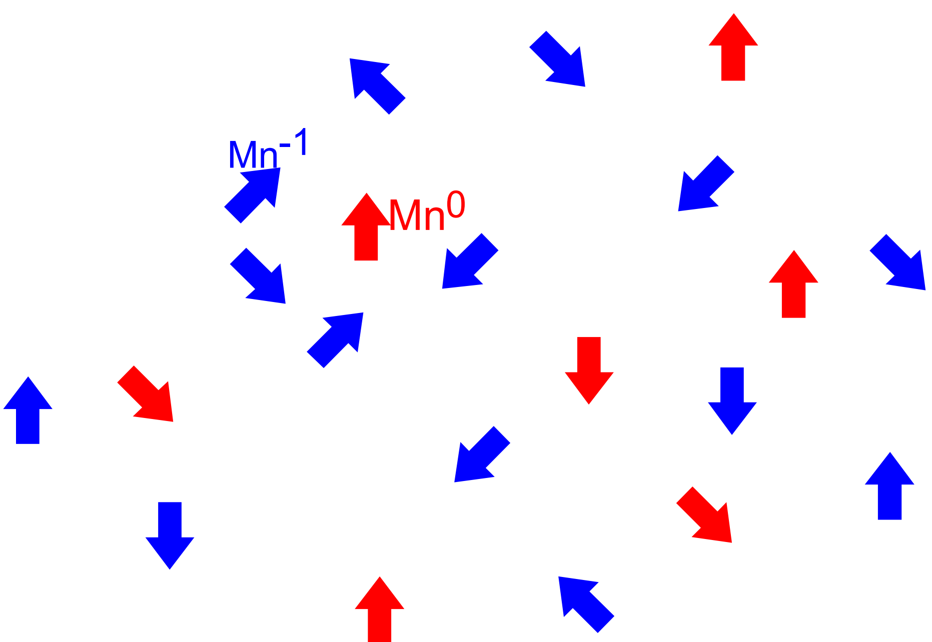


Ferromagnetic triplet

$$E_s = -2\,|J|$$

FM order from two-color percolation

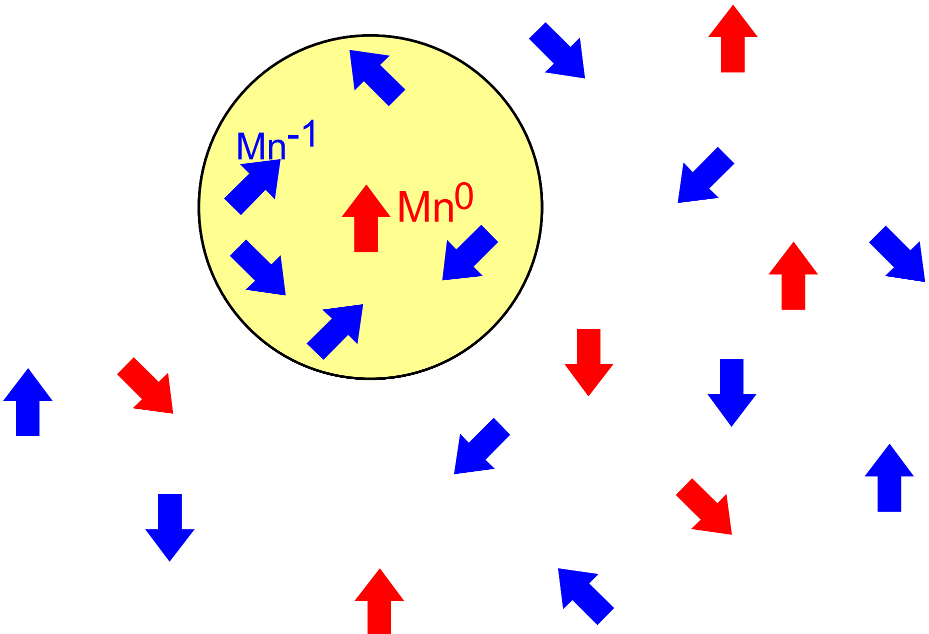
1. Randomly oriented Mn spins, each with charge 0 or -1



FM order from two-color percolation

1. Randomly oriented Mn spins, each with charge 0 or -1

2. Spins interact if their wavefunctions overlap



FM order from two-color percolation

1. Randomly oriented Mn spins, each with charge 0 or -1

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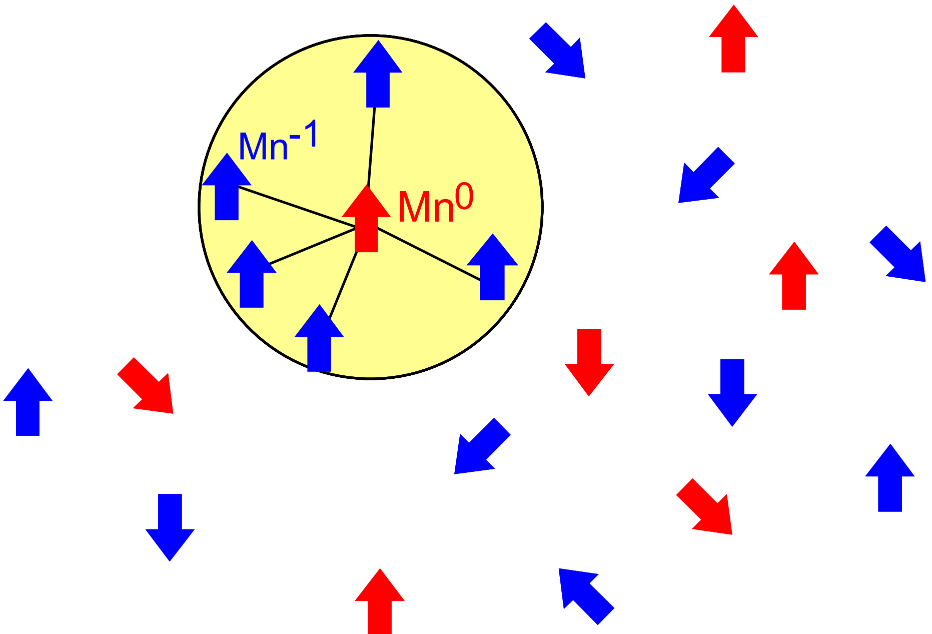
3. Spins with opposite charge interact to form ferromagnetic clusters



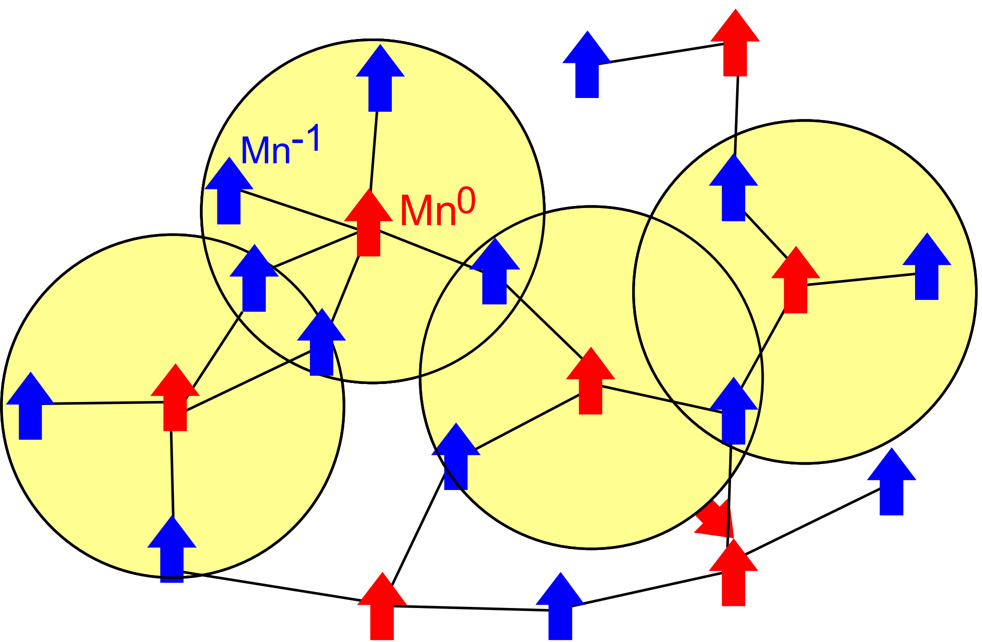
FM order from two-color percolation

1. Randomly oriented Mn spins, each with charge 0 or -1

2. Spins interact if their wavefunctions overlap

3. Spins with opposite charge interact to form ferromagnetic clusters

4. If clusters are larger than the percolation threshold, the entire spin system becomes ferromagnetic

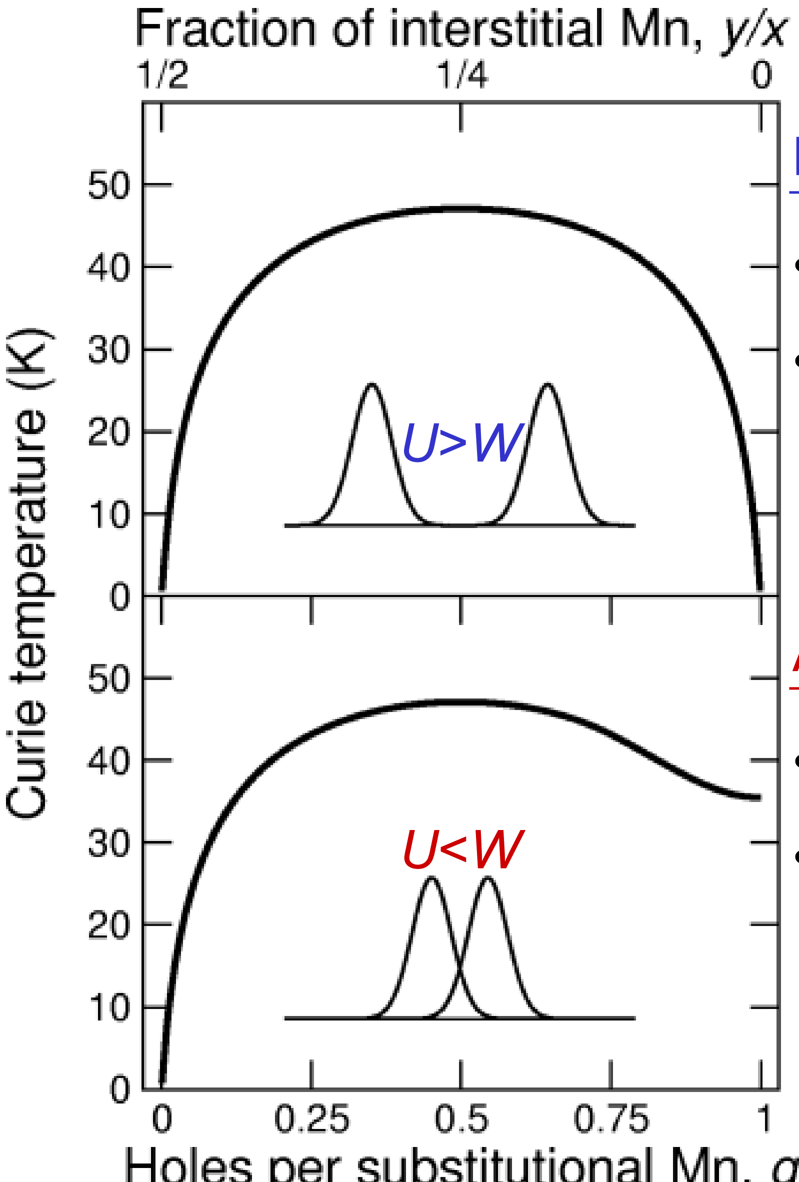


$$R_{perc} \propto \left(\frac{1}{\sqrt{q(1-q)}}\right)^{1/3}$$

diverges when:

all Mn^0 (zero comp)	all Mn^{-1} (complete comp)

Curie temperature vs. compensation



Mott-Hubbard insulator

- Zero compensation: T_c=0 !
- Curie temperature highest for q=0.5

Anderson localization

- Zero compensation: T_c suppressed !
- Curie temperature highest for q=0.5

Below the metal-insulator transition, partial compensation in Mn-doped semiconductors <u>promotes</u> ferromagnetism!

Lessons Learned

1. Convergence is not the same as completeness.
2. Completeness is impossible, but one must try.
3. DFT can’t do everything!

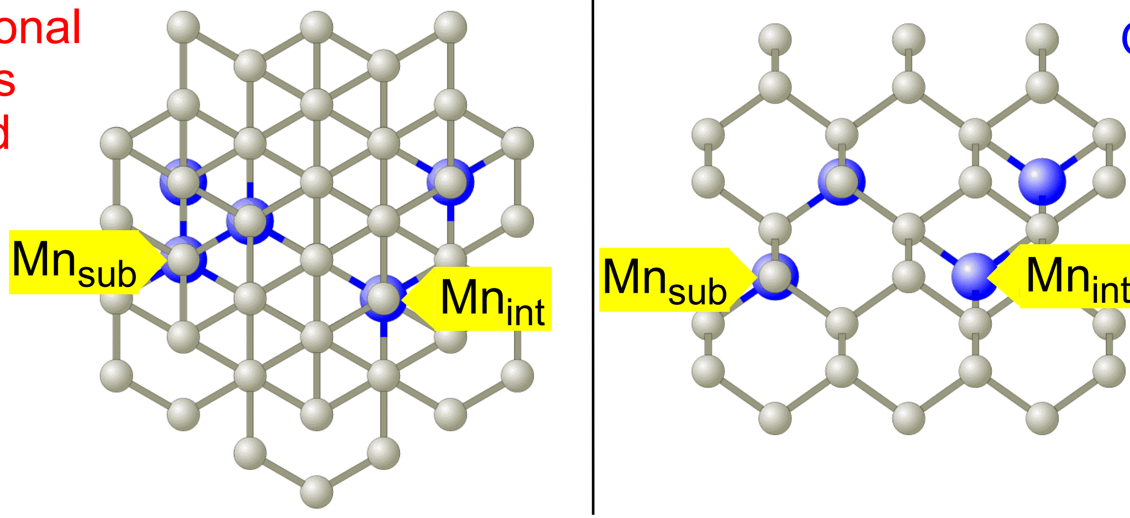
Experimental evidence for interstitial Mn

View along <111>

View along <110>

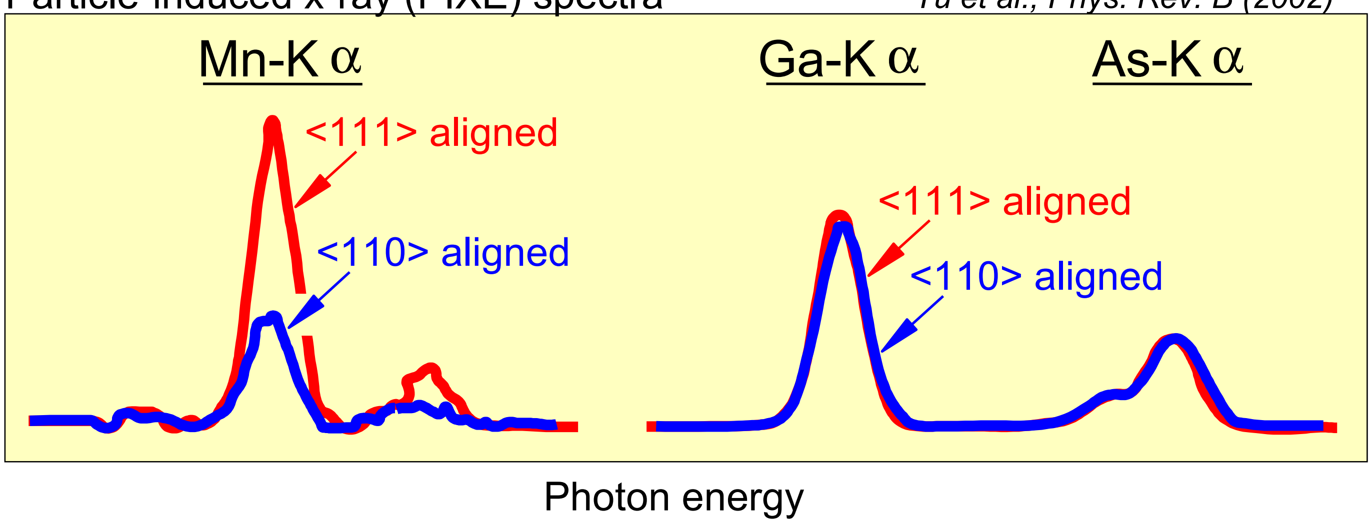
Both substitutional and interstitials are shadowed

Only substitutionals are shadowed

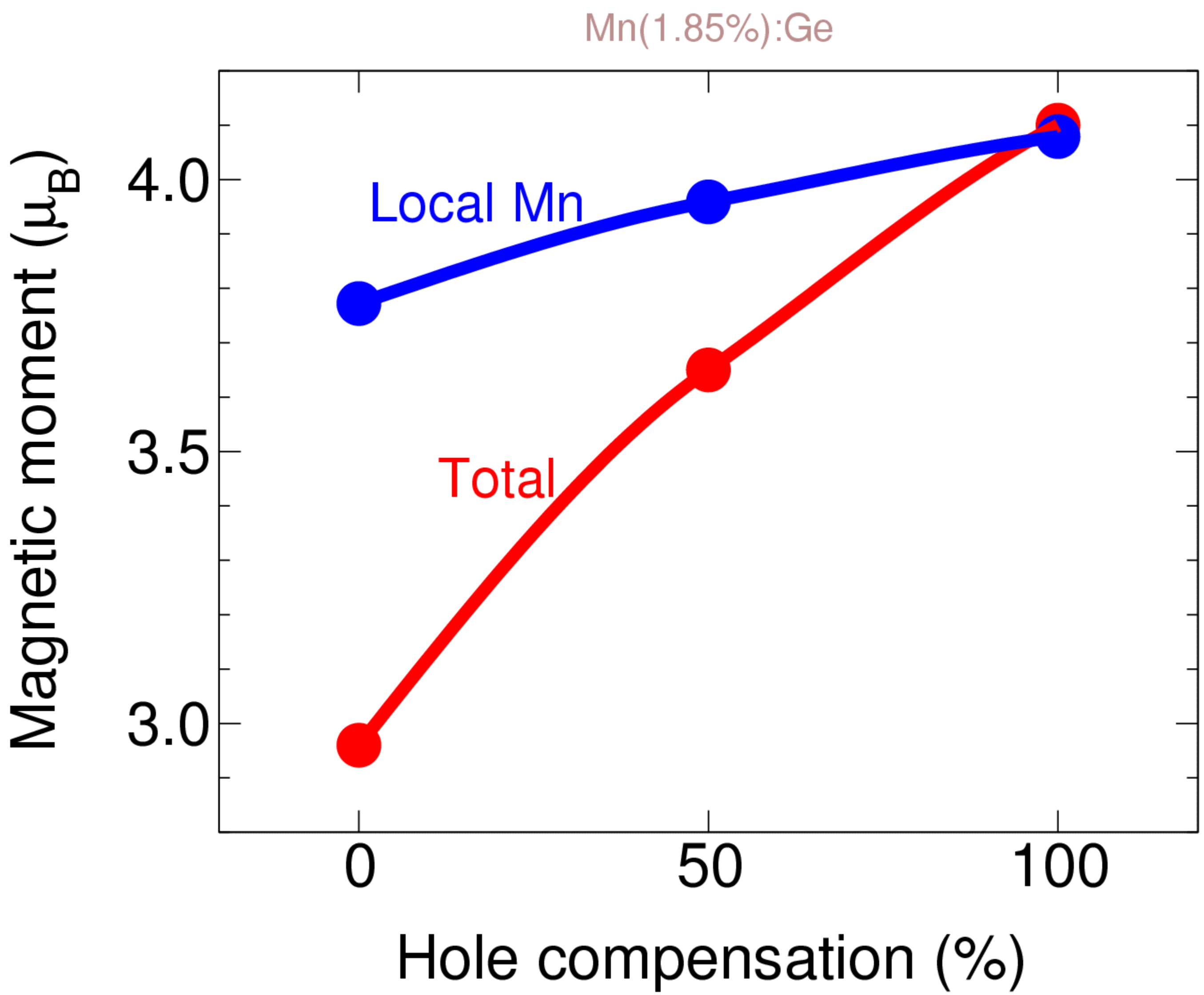


Particle-induced x-ray (PIXE) spectra

Yu et al., Phys. Rev. B (2002)



The role of compensation: Mn moment



Compensation suppresses the holes